DP-MS-78-29

ALPHA AND BETA RADIOLYSIS OF PLUTONIUM HEXAFLUORIDE VAPOR

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Paper presented at the
176th National Meeting of the American Chemical Society
Miami Beach, Florida
September 10-15, 1978

Also proposed for publication in the
Journal of Physical Chemistry

Text pages: 28
Tables: 7
Figures: 9

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

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ABSTRACT

The alpha and beta radiolysis of PuF_6 vapor was studied at 22°C in passivated aluminum vessels at pressures from 5 to 50 torr. The plutonium itself served as the radiation source. For alpha radiolysis, plutonium that was 4.8% ^{238}Pu was used to prepare the PuF_6. For beta radiolysis, the plutonium was 75% ^{241}Pu. PuF_6 decomposition rates were measured from the UV absorbance of the PuF_6. The amount of alpha and beta energy absorbed was calculated from stopping powers for PuF_6. With alpha radiolysis, the decomposition followed a first order reversible mechanism, indicating a back reaction between the products F_2 and PuF_4. The G value for the alpha particle decomposition of PuF_6, $G(-PuF_6)$, was 2.2 ±0.7 molecules/100 eV. With beta radiolysis, the decomposition rate was dependent only on the dose rate; evidence for the back reaction was not observed. For beta decomposition, $G(-PuF_6)$ was 1.0 ±0.3 molecules/100 eV. The difference between the G values may be due to the higher fraction of alpha energy compared to beta energy being absorbed at the wall of the reaction vessel. $G(-PuF_6)$ for beta radiolysis was independent of PuF_6 pressure and dose rate. $G(-PuF_6)$ for alpha was less precise but did not exhibit a significant effect of pressure.

INTRODUCTION

Plutonium hexafluoride, because of its appreciable vapor pressure at room temperature (90 torr at 23°C),[1] is a compound that has potential application in the nuclear industry. For example, this relatively high vapor pressure is the basis for the fluoride volatility process for separating plutonium and uranium from fission products in spent nuclear fuel.[2] Two problems in handling PuF_6 are its high chemical reactivity and its radiolytic instability. PuF_6 is an excellent fluorinating agent and reacts rapidly, and under some conditions violently, with many materials such as H_2O and organic compounds. Also, because of the radioactivity of plutonium isotopes, PuF_6 continuously decomposes.

Previous studies of the radiolysis of PuF_6 have been performed.[3-7] These studies have shown that the products of alpha radiolysis[3-5] of solid PuF_6 and of gamma radiolysis[6] of the vapor are nonvolatile PuF_4 and gaseous F_2. Studies of the alpha radiolysis[4,5,7] of the vapor have established that the radiolytic decomposition rate is slower in the vapor than in the solid phase, and that the rate decreased with radiation dose or when PuF_4 was present.[7] However, these alpha radiolysis studies did not determine a value for $G(-PuF_6)$, the G value for decomposition of the vapor. This quantity is necessary to calculate the radiolytic decomposition of the vapor in various process conditions.

The purpose of the present work was to determine $G(-PuF_6)$ for PuF_6 vapor for both alpha and beta radiolysis. These two types of radiation are emitted by plutonium isotopes and would be responsible for nearly all of the radiolytic decomposition of PuF_6 vapor in a process. $G(-PuF_6)$ was not determined in the previous alpha radiolysis studies for two reasons. First, it was not certain at that time whether nonradiolytic thermal reactions were also contributing to the decomposition.[5] Second, a rigorous calculation of amount of energy absorbed by the PuF_6 vapor from the alpha particles was not possible.

In the present study, the possible effect of thermal decomposition was excluded by studying the radiolytic decomposition at several high dose rates. These dose rates were achieved for alpha radiolysis by using PuF_6 prepared by fluorinating plutonium that contained added ^{238}Pu, an intense alpha emitter. The value of $G(-PuF_6)$ obtained at these dose rates was compared to that calculated from data obtained at a much lower dose rate where it was thought that a thermal reaction might be contributing to the decomposition. Beta radiolysis was studied at high dose rates by using PuF_6 that contained a large fraction of ^{241}Pu, an intense beta emitter. The amount of energy absorbed by the PuF_6 from radioactive decay of the plutonium was calculated from the isotopic content of the plutonium, the size of the radiolysis vessel, the pressure of PuF_6, and estimated stopping powers of PuF_6 for alpha and beta particles from plutonium. During alpha or beta radiolysis,

the concentration of PuF_6 was determined by its UV absorbance. With this method of analysis, PuF_6 did not have to be separated from its decomposition products as in the previous studies.

Experimental Section

PuF_6 Preparation. PuF_6 was prepared by exposing a mixture of PuO_2 and PuF_4 of the desired plutonium isotopic content to flowing F_2 at 575°C for 4-6 hours. The vacuum system and furnace were previously cleaned and passivated by exposure to 500 torr F_2 at 100°C. The F_2-PuF_6 mixture from the furnace was passed through a trap cooled by a dry ice slurry to condense PuF_6. Excess F_2 was collected on Al_2O_3 traps. The PuF_6 product was further purified by degassing it at -79°C. It was then sublimed into a 5-liter nickel vessel. Prior to each time that PuF_6 was removed from the vessel, F_2 that had accumulated from radiolysis of the PuF_6 during storage was removed by a least two freeze-pump-thaw cycles of the PuF_6.

Isotopic Composition of the PuF_6. Three different isotopic compositions of plutonium were used in this study (Table I). Because of these compositions, different alpha and beta emission rates were obtained (rows 6 and 7 in Table I). Plutonium compositions were determined by mass spectrometric analysis of the PuO_2F_2 formed by reaction of moist air with PuF_6 that had previously been expanded into a clean steel test tube. The PuF_4·PuO_2 starting mixture of the desired plutonium isotopic content was prepared by mixing appropriate quantities of plutonium oxides or fluorides

that were primarily 94% ^{239}Pu, 81% ^{238}Pu, or 93% ^{241}Pu. The alpha and beta emission rates in Table I were calculated from the nuclear decay data in Table II.

Radiolysis Vessel. The radiolysis vessel was a cylindrical (10.1 cm ID × 13.5 cm tall) 1.09-liter aluminum vessel with a quartz optical cell on either end. Gases could be introduced or removed through two valves on one end. All the valves had packless brass bellows with metal seats. Each vessel and associated valves, fittings, and cells were carefully cleaned and leak checked. The vessels and valves were passivated by exposure to 600 torr F_2 at 100°C for 16 hours and to 30-50 torr PuF_6 (containing 93% ^{239}Pu) at ambient temperature. The quartz cells were dried at 500°C but were not exposed to F_2 or PuF_6 until they were used for an absorbance reading. Several different vessels were used throughout the study.

Test Procedure. Immediately before a vessel was filled with PuF_6 for a radiolysis experiment, the PuF_6 in the storage container was purified by at least two freeze-pump-thaw cycles. PuF_6 at a known pressure was then expanded into the vessel. PuF_6 was not expanded into the cells until time for an absorbance reading. This ensured that during radiolysis the PuF_6 was exposed only to passivated aluminum surfaces, and to the small amount of brass in the valves. Pressures were measured by either a 0-10 torr or a 0-100 torr calibrated pressure transmitter. After the vessel was filled, it was removed from the vacuum line and stored to allow

radiolytic decomposition to occur. After various time intervals, PuF_6 was expanded into a cell and the absorbance due to PuF_6 was measured. From this measurement, the pressure of PuF_6 in the vessel was calculated. After the measurement, the valve between the cell and vessel was again closed. The volume of the cell and connector was <10 milliliters; thus <1% of the contents of the vessel was removed for each reading. After both cells had been used, the vessel was again attached to the vacuum line and the final total pressure in the vessel was measured. The undecomposed PuF_6 in the vessel and cells was then purified and returned to the storage container. In several cases, the vessel was then filled for another test.

Absorbance Measurements. The absorbance of the PuF_6 was measured with a Coleman Model 101 spectrophotometer in the glove box. The spectrum of PuF_6 determined with this instrument agreed with that determined by Steindler and Gunther.[10] In the radiolysis tests, the absorbance was measured at 516 nm for pressures of 0-10 torr, and 365 nm for higher pressures. First the absorbance of the empty cell was measured. Then PuF_6 was allowed to expand into the cell, and readings were taken until the absorbance became constant. This usually required 15 to 20 minutes. The valve separating the cell and vessel was then closed.

To test whether the absorbance followed the Beer-Lambert law, readings were taken immediately after several PuF_6 samples at several known pressures had been expanded into the vessels. Results were good at both wavelengths. The molar absorptivities calculated from the ideal gas law and slopes of the linear absorbance vs PuF_6 pressure plots were $1039 M^{-1} cm^{-1}$ at 316 nm and $194 M^{-1} cm^{-1}$ at 365 nm. The value at 316 nm differed by only 1.5% from that determined by Steindler and Gunther.[10] At 316 and 365 nm, the molar absorptions for F_2 are 5 and $1 M^{-1} cm^{-1}$, respectively;[11] thus, separation from F_2 was not necessary. PuF_6 slowly decomposed over a period of days in the cells and caused them to become cloudy after extended use. Apparently, the PuF_6 hydrolyzed to form PuO_2F_2 or reacted with the quartz. This type of reaction of PuF_6 in quartz cells has been observed previously.[10] In the radiolysis experiments, the absorbance of this film was included in the absorbance measurement taken before PuF_6 was allowed to enter the cell. When the absorbance of the empty cell became too high, the cell was removed. It was cleaned with dilute HNO_3, dried at 500°C, and then replaced. The cell was then evacuated and the vessel was repassivated with PuF_6.

Calculation of Energy Absorbed by PuF_6. The amount of alpha and beta energy absorbed by the PuF_6 was calculated from the alpha and beta energy emitted by decay of the plutonium isotopes and the fraction of this energy absorbed. The amount emitted was calculated from the isotopic content of the plutonium. The fraction absorbed was calculated from an equation for the energy loss by an alpha or beta particle as it traveled through the PuF_6. To determine this total energy loss per particle, the equation was integrated over all straight line distances from within the vessel to the wall of the vessel. The fraction was then calculated knowing the initial energy of the particle. For the integration, the vessel was assumed to be a sphere of volume equal to that of the cylindrical vessel. This assumption is justified because the height and diameter of the cylinder were nearly equal.[12]

The equation for energy loss by the alpha particles was derived from calculated stopping powers for PuF_6 for the 5.4-MeV alpha particles of ^{238}Pu. These were the most abundant alpha particles irradiating the PuF_6 in the radiolysis experiments. Exact stopping powers for PuF_6 could not be calculated because those for plutonium are unavailable. However, stopping powers for uranium and fluorine have been calculated by Williamson et al.[13] It was assumed that those for PuF_6 were equal to those for UF_6. This assumption does not introduce significant error because of the similar electronic structures of uranium and plutonium. A maximum uncertainty of 20% has been assigned to the stopping

powers calculated for uranium and fluorine.[13] The range of the 5.4-MeV alpha particles in PuF_6 was then derived by numerical integration of the inverse of these stopping powers. At STP, the calculated range was 0.0109 g/cm^2 (6.92 mm). The fraction of energy absorbed as a function of pressure up to 50 torr at 21°C is shown in Figure 1. Because this fraction is small, the large energy loss rates by the alpha particles at the end of their range were not significant and the alpha particles could be assumed to be traveling in nearly straight lines in the vessel. As shown in Figure 1, this fraction increases almost linearly with pressure.

The equation for energy loss by ^{241}Pu beta particles also could not be calculated exactly. This equation was derived from data for the distribution of absorbed doses in water from beta particles around a point source of ^{3}H. This distribution was calculated by Berger.[14] The average energy of these beta particles (5.69 keV)[15] is very close to that for beta particles from ^{241}Pu (6.0 keV). The results of Berger[14] were modified slightly to account for this difference. The distribution in water was converted to PuF_6 by the method of Cross[16] with effective atomic numbers of the respective media. As expected, the fractions of beta energy absorbed were much higher than those for the alpha particles (Figure 1).

Fractions of alpha and beta energy absorbed by PuF_6 from particles emitted by plutonium on the surface of the vessel were also calculated. These particles also contributed to the total dose absorbed by the PuF_6 depending on the amount of plutonium deposited. On the average, these fractions were a factor of 1.33 larger than those in Figure 2. This factor results because the average distance traveled by particles emitted from the inside surface of a sphere before striking the sphere is equal to the radius of the sphere. For particles emitted from within the sphere and not on the surface, this distance is three-fourths of the radius.[12] For the particles emitted from plutonium on the wall, the fraction escaping the wall and the PuF_4 film deposited on the wall was then calculated as a function of thickness of the PuF_4 film. This fraction (Figure 2) has a maximum of 0.5 because half the alpha or beta particles are emitted into a wall. A crystalline density of 5 g/cm^3 was assumed for the PuF_4.

Results and Discussion

Stoichiometry. Results in this study have substantiated that the products of the alpha and beta radiolysis of PuF_6 vapor are PuF_4 and F_2. In some of the alpha radiolysis tests, a sample of the solid decomposition product was removed from the inside vessel wall after radiolysis and was analyzed by x-ray diffraction. A pattern corresponding to crystalline $PuF_4 \cdot 1.5\ H_2O$ was obtained.[17] Three other broad peaks were also found and were assigned to anhydrous PuF_4 based on the pattern for anhydrous PuF_4 prepared by W. C. Mosley in this laboratory.[18] No other bands were observed.

In the beta radiolysis experiments where the final pressure was measured (Table V, columns 1 and 3 of representative data), the total pressure remained unchanged indicating that for each mole of PuF_6 decomposed one mole of gas was produced. These two results (the x-ray analysis and unchanging pressure) substantiate that the decomposition reaction is

$$PuF_{6(g)} \longrightarrow PuF_{4(s)} + F_{2(g)}$$

As indicated earlier, other studies have shown that this is also the reaction for alpha radiolysis of the solid,[3-5] and for gamma radiolysis of the vapor.[6]

Alpha Radiolysis Kinetics. PuF_6 pressure decreases at five different initial pressures with PuF_6 containing plutonium that was 4.3% ^{238}Pu are shown in Figure 3. Based on the isotopic composition of this plutonium indicated in Table I, the decomposition indicated in Figure 3 is due to alpha radiolysis. Data for these experiments are given in Table III. At the three higher pressures, the rate of decomposition decreases with time as indicated by the nonlinearity of the data. Three factors could cause this rate decrease. One factor is the decrease in dose rate due to loss of plutonium to the vessel walls as PuF_4. Once plutonium is on the wall as PuF_4, only half of its alpha particles irradiate the PuF_6 vapor. A second factor is the dose rate decrease due to the PuF_6 pressure decrease. As the PuF_6 pressure decreases, the fraction of alpha energy absorbed decreases even if the alpha flux were constant (Figure 1). The third factor is that as F_2 and PuF_4

accumulate, a back reaction that forms PuF_6 may be initiated. Evidence for this reaction has been found by gamma radiolysis of mixtures of F_2 and PuF_4, and also by UV excitation of such mixtures.[6,19]

The decrease in dose rate due to PuF_4 being deposited on the vessel walls is not sufficient to cause the observed rate decrease. Calculations based on data in Table III showed that the maximum decrease in dose rate because of this factor was only 8%. From the initial and final slopes of the curves in Figure 3, the decomposition rates are estimated to decrease by more than 70%.

If the dose rate decrease due to the PuF_6 pressure decrease were the major factor causing the decrease in decomposition rate, then the decomposition rate should be first order with respect to the PuF_6 pressure. This relationship results because over the pressure decrease in any one experiment, the fraction of alpha energy absorbed by the PuF_6 gas decreases almost linearly with pressure (Figure 1). A plot of log PuF_6 pressure versus time was clearly nonlinear indicating that first order kinetics were not followed and that this dose rate decrease was not the most significant factor causing curvature in Figure 3.

Apparently, the back reaction between PuF_4 and F_2 is the most important factor. When this reaction between F_2 and PuF_4 is considered, the overall reaction for PuF_6 radiolysis is

$$PuF_6 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} PuF_4 + F_2$$

The rate equation for the pressure decrease is then

$$-\frac{dP_{PuF_6}}{dt} = k_f P_{PuF_6} - k_r P_{F_2} \qquad (1)$$

where P_{PuF_6} and P_{F_2} are the pressures of PuF_6 and F_2, respectively. Since the total pressure is constant during radiolysis,

$$P_{F_2} = P_{o_{PuF_6}} - P_{PuF_6} \qquad (2)$$

where $P_{o_{PuF_6}}$ is the initial PuF_6 pressure. The rate expression is then

$$-\frac{dP_{PuF_6}}{dt} = k_f P_{PuF_6} - k_r (P_{o_{PuF_6}} - P_{PuF_6}) \qquad (3)$$

Integration gives

$$\ln[(k_f + k_r)P_{PuF_6} - k_r P_{o_{PuF_6}}] = -(k_f + k_r)t + \ln(k_f P_{o_{PuF_6}}) \qquad (4)$$

A nonlinear least squares analysis was used to determine if the data in Figure 3 fit this equation and to calculate values for k_f and k_r. As the linear plots in Figure 4 indicate, the equation described the data very well. The calculated values for k_f and k_r are included in Table III. The method for calculating the G values in column 8 of Table III is described in the next section.

At the two lower pressures in Figure 3, the pressure decreased linearly with time. Thus, extremely small values were calculated for k_r. In these two cases, the data fit a simple first order rate equation. The irradiations were not long enough to determine when the back reaction became significant. It is apparent that the back reaction is not as significant at the lower pressures as at the higher pressures, even when the relative partial pressures of PuF_6 and F_2 present at the termination of the experiments are similar. Thus, the rate of the back reaction must be dependent on some factor other than the F_2 pressure. Perhaps the dose rate or some other factor is significant.

G Values for Alpha Radiolysis. The G value for the alpha-induced decomposition of PuF_6 vapor can be calculated from the values for k_f. The rate of the forward reaction in terms of the G value is

$$-\frac{dP_{PuF_6}}{dt} = \frac{G(-PuF_6)}{100} \frac{RT}{NV}\left(\frac{dE}{dt}\right)_{PuF_6} \qquad (5)$$

where

R = ideal gas law constant

T = radiolysis temperature, 21 ± 1°C

N = Avogadro's number

V = volume of the radiolysis vessel, 1.09 L

$\left(\frac{dE}{dt}\right)_{PuF_6}$ = rate of energy absorption by PuF_6

As indicated earlier, the rate of energy absorption by PuF_6 is equal to the rate of alpha and beta energy production by decay of the plutonium times the fraction of this energy absorbed. In the experiments with plutonium containing 4.8% ^{238}Pu, the beta rate was negligible compared to the alpha rate. At the PuF_6 pressures in the experiments, the fraction of alpha radiation absorbed over the small pressure change in any one experiment varies linearly with pressure (Figure 1); thus,

$$\left(\frac{dE}{dt}\right)_{PuF_6} = C(P)\ P_{PuF_6}\ \frac{dI}{dt} \qquad (6)$$

where

$C(P)$ = slope of Figure 1 over the appropriate pressure range and is the fraction absorbed per unit pressure

$\frac{dI}{dt}$ = rate of alpha energy produced by decay of plutonium isotopes present

The expression for the decomposition rate is then

$$-\frac{dP_{PuF_6}}{dt} = \frac{G(-PuF_6)}{100}\ \frac{RT}{NV}\ C(P)\ P_{PuF_6}\ \frac{dI}{dt} \qquad (7)$$

From eq 1, the rate of decomposition is also given by $k_f P_{PuF_6}$. Setting these two expression equal gives

$$k_f = \frac{G(-PuF_6)}{100}\ \frac{RT}{NV}\ C(P)\ \frac{dI}{dt} \qquad (8)$$

After rearrangement,

$$G(-PuF_6) = k_f\ \frac{100\ NV}{RT\ C(P)}\ \frac{dt}{dI} \qquad (9)$$

The factor [1/C(P)][(dt/dI)] is the inverse of the sum of dose rate contributions per unit pressure from alpha particles from plutonium in the gas phase and from plutonium deposited on the walls. Also the alpha particles emanating from plutonium on the walls are affected by the thickness of the PuF_4 film on the walls. The expression for the total absorbed dose rate per unit pressure is then

$$C(P)\frac{dI}{dt} = C(P)_g \left(\frac{dI}{dt}\right)_g + f_\alpha\, C(P)_w \left(\frac{dI}{dt}\right)_w \qquad (10)$$

The subscripts g and w indicate whether the gas or wall is being considered. f_α is the fraction of alpha particles from plutonium on the wall that escape absorption by the wall or by PuF_4 on the wall.

The quantity f_α was determined from Figure 2 and from the known amount of PuF_4 deposited on the wall from previous experiments in that specific vessel. The thickness of the PuF_4 was calculated by assuming that PuF_4 was deposited homogeneously over all the vessel wall. $C(P)_g$ was determined from the slope of the appropriate curve in Figure 1 over the pressure change in the experiment. $C(P)_w$ was 1.33 times $C(P)_g$ because of the longer average distance traveled by alpha particles from the wall.

The dose rate contribution for plutonium deposited on the walls during passivation with PuF_6 containing 93% ^{239}Pu was negligible. This was because of the low alpha and beta emission rates of this plutonium (Table I) and the small amount

deposited. Although the exact amount of this plutonium was not determined, it was estimated to be less than 100 $\mu g/cm^2$. This estimation is based on data presented by Steindler.[20] Only 1.6 $\mu g/cm^2$ was deposited when prefluorinated aluminum was exposed to 42 torr PuF_6 for 1 hour.[20] The PuF_6 consumption depended approximately on $(time)^{1/2}$. Thus, an exposure of ~24 hours, as in the present study, would deposit <10 $\mu g/cm^2$. But even if 100 $\mu g/cm^2$ was deposited, this plutonium would contribute only 0.5% to the total dose rate.

The total calculated dose rates and the fraction of this dose rate orginating at the walls are given in Table III. At the pressures of these experiments, the fraction of alpha energy absorbed by the PuF_6 vapor varied from 36% to 5%. Thus, in all cases, more of the alpha energy was absorbed by the walls or by PuF_4 on the walls rather than by PuF_6 vapor.

The average value for $G(-PuF_6)$ for the five experiments is 2.0 ± 0.9 molecules/100 eV. Although there is considerable scatter in the results, it appears that $G(-PuF_6)$ is not significantly affected by pressures between 9 and 50 torr.

Data for six other alpha radiolysis experiments are given in Table IV. In these experiments, the PuF_6 decomposition was measured at only one time rather than two as in the experiments described above. Consequently, independent values for k_f and k_r could not be calculated from the data. To determine k_f, values for k_r in these experiments were estimated from the previous

experiments. k_f was then calculated from eq 4 with the initial PuF_6 pressure and the PuF_6 pressure at the one decomposition time. For the experiments at the four higher pressures in Table IV, k_r values were estimated from Figure 5, which is a plot of the dose rate dependency of k_r found in the earlier experiments. At initial pressures of 10.1 and 7.7 torr, k_r was assumed to be negligibly small as it was at low pressures in the other results. At these two pressures, k_f was calculated from a simple first order rate law. As with the other experiments, a significant fraction of the dose rate in many cases resulted from plutonium on the walls. Also based on the PuF_6 pressures, the fraction of alpha energy absorbed by the vapor ranged from 34% to 4.7% indicating that more of the energy was deposited at the vessel wall. The average value for $G(-PuF_6)$ in these experiments is 2.3. This agrees with that found in the earlier experiments.

The average for $G(-PuF_6)$ for all the alpha radiolysis experiments is 2.2 ±0.7 molecules/100 eV. This is close to the value of 3.3 determined by Weinstock and Malm[5] for alpha radiolysis of the solid. A value of 7.5 ±1.7 has been determined for gamma radiolysis of the vapor at 60 to 70°C.[6] The reason for the higher value with gamma radiolysis is not known. Perhaps it is partly due to the higher temperature of the gamma radiolysis experiments. Also, a surface effect may be present in the gamma radiolysis since the gamma rays interact with the reaction vessel as well as the

gaseous PuF_6. It would be helpful if gamma and alpha radiolysis experiments were performed at equal temperatures. For the alpha radiolysis of UF_6,[21] a volatile fluoride that is similar to but more stable than PuF_6, a value of 0.90 ± 0.73 has been reported for $G(-UF_6)$. In that study,[21] it was also found that the rate of decomposition followed a first order reversible mechanism as with PuF_6.

Because the value for $G(-PuF_6)$ is independent of dose rate, nonradiolytic thermal processes must not be affecting the decomposition. If thermally induced reactions were affecting the decomposition, larger G values would be expected at the lower dose rates where their contribution would be more significant. Results of Tsujimura and coworkers [22] substantiate that thermal decomposition should not be a factor at 21°C. They found no thermal decomposition when up to 80 torr of PuF_6 was heated to 120°C for one hour. At higher temperatures, they determined an activation energy for the thermal decomposition of 14.8 kcal/mole. With this activation energy, one hour at 120°C corresponds to 25 days at 22°C. Thus, thermal decomposition would not be expected at 22°C until more than 25 days had elapsed. Because of the high alpha dose rate, all but one of the alpha radiolysis experiments in this work were shorter than 25 days.

Beta Radiolysis Kinetics. PuF_6 pressure decreases at eight different initial pressures with PuF_6 containing plutonium that was 73% ^{241}Pu are shown in Figure 6. Because the beta emission

rate is higher than the alpha for plutonium of this isotopic composition (Table I), and because much higher fractions of the beta energy are absorbed (Figure 1), beta radiolysis accounted for greater than 90% of the PuF_6 decomposition depicted in Figure 6. Data and results for these experiments are given in Table V.

With beta radiolysis, the pressure decreased linearly at all the pressures. This result is in contrast to that obtained with alpha radiolysis. Apparently, the reverse of the decomposition reaction is less effective with beta than with alpha radiation. This reaction was less effective even though the relative partial pressures of F_2 and PuF_6 were similar at the end of both the alpha and beta experiments. Also, the total pressure is not a factor in this case, since the alpha and beta experiments were performed over nearly identical pressure ranges.

Two possible factors that could influence the reverse reaction are the amount of energy deposited at the wall and the dose rate. In the alpha radiolysis experiments, more energy was deposited at the vessel walls than was absorbed by the PuF_6 vapor. In all alpha radiolysis experiments, less than 35% of the energy was absorbed by the vapor. Since PuF_4 is on the vessel walls and is a reactant in the reverse action, the higher fraction of energy deposition at the walls may have made the reverse reaction competitive with the forward. In the beta radiolysis experiments, greater than 75% of the energy was absorbed by the vapor. Because of the lower fraction absorbed

by PuF_4 on the walls, the reverse reaction may not have been as effective as in the alpha radiolysis experiments. However, since the beta radiolysis experiments were at a lower dose rate than the alpha radiolysis experiments in which the reverse reaction was effective, dose rate cannot be excluded as a possible factor.

With beta radiolysis at these pressures, dose rates, and percent decompositions, the decomposition rate does not follow a first order reversible mechanism as it does with alpha radiolysis. Also, simple first order kinetics are not applicable since at most of the pressures, the fraction of beta energy absorbed did not vary significantly with the PuF_6 pressure (Figure 1). Only in the experiment at 5.04 torr did this fraction vary by more than 10% during the experiment. In that experiment, the fraction absorbed dropped from 0.81 at 5.04 torr to 0.59 at the final PuF_6 pressure (2.09 torr). Reason for the lack of some curvature in the data for this experiment is unknown unless there is some energy transfer from F_2 to PuF_6. From the above, it is concluded that in beta radiolysis the decomposition rate depends only on the absorbed dose rate. In the experiments except that at 5.04 torr, this absorbed dose rate did not vary more than 15%. This variation resulted from slight changes in the fraction of beta energy absorbed, and from loss of plutonium from the vapor phase to the vessel walls as with alpha radiolysis.

G Values for Beta Radiolysis. The rate of decomposition of PuF_6 is given by eq 5. In the beta radiolysis experiments, the

total rate of energy absorption by PuF_6 is

$$\left(\frac{dE}{dt}\right)_{PuF_6} = F_{\beta,w} f_\beta \left(\frac{dI}{dt}\right)_{\beta,w} + F_{\beta,g}\left(\frac{dI}{dt}\right)_{\beta,g} + C(P)_g P_{PuF_6}\left(\frac{dI}{dt}\right)_{\alpha,g} + C(P)_w P_{PuF_6}\left(\frac{dI}{dt}\right)_{\alpha,w} \quad (11)$$

The subscripts β and α indicate whether beta or alpha radiation is being considered. The subscripts g and w indicate plutonium in the gas phase or on the wall. Also

$F_{\beta,w}$ = fraction of beta energy absorbed by PuF_6 from beta particles emitted from plutonium on the wall

$F_{\beta,g}$ = fraction of beta particles absorbed by PuF_6 from beta particles emitted by plutonium in the gas phase

f_β = fraction of beta particles emitted from plutonium on the wall that escape absorption by the wall or the PuF_4 film

Because of the low alpha emission rate and the small values for $C(P)\cdot P_{PuF_6}$ (fraction of alpha energy absorbed) compared to $F_{\beta,g}$ and $F_{\beta,w}$, the last two terms in eq 11 contribute only a small fraction of the total dose rate. For completeness, however, all four terms in eq 11 were calculated, and the sum was used for the total dose rate. The fraction of this rate that resulted from alpha energy was less than 7% in all the experiments. Also, the fraction of absorbed energy coming from the wall was small except in the experiment at 5.04 torr where considerable plutonium containing 73% ^{241}Pu was on the wall from a previous experiment in that vessel. As with alpha radiolysis, the amount of absorbed energy from plutonium containing 93% ^{239}Pu that was deposited by

passivation was negligible. Again if the presumed 100 $\mu g/cm^2$ were deposited, the dose rate from this plutonium would be less than 0.3% of the lowest dose rate in Table V.

The decomposition rates (torr/day) were calculated by linear least squares determination of the slopes in Figure 6. G values (column 8) were then calculated by eq 5 with the dose rate calculated from eq 11.

Five other beta radiolysis experiments were performed in which the PuF_6 pressure was measured after only one decomposition time. For these, G values were calculated from the initial and final pressures as described above. Data and results are in Table VI.

Because the contribution of alpha energy to the total dose rate in the data in Tables V and VI is small, the calculated G values are equal to the G values for beta radiolysis. The average value is 1.0 ±0.3 molecules/100 eV. As with alpha radiolysis, there is no effect of pressure or dose rate on $G(-PuF_6)$. Because of absence of a dose rate effect, nonradiolytic thermal decomposition processes are not significant. $G(-PuF_6)$ for beta radiolysis is a factor of 2.2 smaller than that for alpha radiolysis.

Analysis of Other Alpha Radiolysis Data. Steindler and coworkers[7] have published data for the radiolytic decomposition of PuF_6 vapor at 26°C and at initial pressures of 50 and 100 torr. They did not determine G values because at that time data were not available for estimating stopping powers for PuF_6. Decomposition rates were presented as percent PuF_6 decomposed

per day for experiments lasting up to 571 days. We have analyzed their data further and have calculated values for $G(-PuF_6)$ from their data. The results agree with results of the present work.

The experiments of Steindler and coworkers were performed in prefluorinated 127 cm^3 spherical nickel vessels.[7] As indicated in Figure 7. equilibrium pressures of F_2 and PuF_6 were attained. This confirms the existence of the reversible mechanism. At equilibrium, the relative partial pressure of F_2 is larger for the experiment with the smaller initial pressure of PuF_6. This indicates that the reverse reaction is less efficient for lower total pressures even though the relative amounts of F_2 and PuF_6 present may be identical.

Values for k_f and k_r were calculated from the data of Steindler et al.[7] by the nonlinear least squares technique. Results (Table VII) indicated that k_r was smaller at the smaller initial PuF_6 pressure. This agrees with the trend for k_r found in the present work (Table III). Figure 8 indicates the excellent correlation of the data with the rate law for a first order reversible mechanism.

Values for $G(-PuF_6)$ calculated from the values for k_f in Table VII were 1.7 at 50 torr and 1.6 at 100 torr. These are within experimental error of the average value for $G(-PuF_6)$ for alpha radiolysis found in present study even though the fractions of alpha energy absorbed by the gases are different and the dose rates are very different. The fraction of energy absorbed by the

PuF_6 in the 0.13-L vessel was 0.33 at 100 torr and 0.15 at 50 torr compared to 0.60 and 0.33 for the 1.09-L vessel. These fractions along with values for C(P) for the two experiments in the 0.13-L vessel were calculated by the method described previously. The alpha flux for 93% ^{239}Pu (Table I) was used to calculate the dose rate. The initial dose rates of 6.32×10^{17} eV(torr·day) at 100 torr and 2.87×10^{17} eV/(torr·day) at 50 torr were used to calculate the G values. These dose rates are 25 to 300 times less than those in the present study. The agreement in the G values from the two studies indicates that nonradiolytic thermal decomposition processes were also not significant in the experiments of Steindler and coworkers.[7]

Comparison of Alpha and Beta G Values. Values for $G(-PuF_6)$ for alpha and beta radiolysis are plotted versus initial PuF_6 pressure in Figure 9. Although the results are somewhat scattered, no significant effect of pressure is indicated. Values for $G(-PuF_6)$ for beta radiolyses are consistently lower than those for alpha radiolysis. We conclude that this difference does not result from an error in calculating the amount of alpha and beta energy absorbed. Reason for the difference is not apparent since LET effects are not expected to be significant at these pressures. Perhaps in the alpha radiolysis, there is an enhanced decomposition at the wall since most of the alpha radiation was absorbed at the wall.

Acknowledgement. I wish to thank three scientists at the Savannah River Laboratory for their contributions to this work. M. K. Jones prepared the PuF_6 that contained plutonium with 4.8% ^{238}Pu. L. M. Arnett and F. E. Driggers developed the computer programs for calculating the alpha and beta energy absorbed. M. J. Steindler of Argonne National Laboratory is thanked for his comments on the manuscript. The information contained in this article was developed during the course of work under Contract No. AT(07-2)-1 with the U. S. Department of Energy.

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TABLE I: Isotopic Composition (wt %) of Plutonium Used to Prepare PuF_6

Isotope	Vessel Passivation	Alpha Radiolysis	Beta Radiolysis
^{238}Pu	0.0061	4.78	0.018
^{239}Pu	93.65	88.6	20.43
^{240}Pu	5.63	5.84	4.34
^{241}Pu	0.69	0.68	72.92
^{242}Pu	0.032	0.13	2.30
Alpha rate, eV/(min•g)	8.15×10^{17}	1.08×10^{19}	3.14×10^{17}
Beta rate, eV/(min•g)	9.27×10^{15}	9.27×10^{15}	9.89×10^{17}

TABLE II: Nuclear Properties of Plutonium Isotopes[a]

Isotope	$T_{1/2}$, yr	Average energy of particles, MeV	
		Alpha	Beta
^{238}Pu	87.8	5.49	0.0
^{239}Pu	2.44×10^4	5.15	0.0
^{240}Pu	6.54×10^3	5.16	0.0
^{241}Pu	14.6[b]	4.90	0.0060[c]
^{242}Pu	3.75×10^5	4.90	0.0

[a] Data from "Chart of the Nuclides," Knolls Atomic Power Laboratory, April 1972, except as noted.

[b] Reference 8; alpha half-life = 4.6×10^5 years.

[c] Calculated from specific power determined in Reference 9 and using a half life of 14.6 years from Reference 8.

TABLE III: Alpha Radiolysis Experiments in Which PuF_6 Decomposition Was Measured at Two Times[a]

PuF_6 pressures, torr		Total decomposition time, days	Initial absorbed dose rate, eV/(torr·day)	Fraction of dose rate from walls, %	k_f, $(days)^{-1}$	k_r, $(days)^{-1}$	$G(-PuF_6)$
Initial	Final						
53.0	47.3	7.9	8.60×10^{19}	6.6	0.0424	0.331	1.8
47.2	41.5	6.4	6.91×10^{19}	<1.0	0.0336	0.168	1.7
35.0	25.5	13.0	5.80×10^{19}	14.8	0.0384	0.0672	2.4
10.4	9.0	29.9	1.56×10^{19}	10.9	-0.00468	$<10^{-8}$	1.1
8.5	6.4	9.0	3.55×10^{19}	67.4	0.0290	$<10^{-8}$	3.1

[a] Plutonium was 4.78% ^{238}Pu; V = 1.09 L; T = 22 ± 1°C.

TABLE IV: Alpha Radiolysis Experiments in Which PuF_6 Decomposition Was Measured at One Time[a]

PuF_6 pressures, torr		Decomposition, time days	Initial absorbed dose rate, eV/(torr•day)	Fraction of dose rate from walls, %	k_f,[b] $(days)^{-1}$	k_r, $(days)^{-1}$	$G(-PuF_6)$
Initial	Final						
50.2	46.5	3.8	7.49×10^{19}	<1.0	0.0313	0.245[c]	1.5
47.5	41.7	3.9	6.55×10^{19}	<1.0	0.0459	0.165[c]	2.5
27.4	22.4	6.7	4.34×10^{19}	13.0	0.0305	0.0334[c]	2.7
22.0	17.3	6.9	3.95×10^{19}	24.0	0.0361	0.01[c]	3.3
10.1	8.9	7.0	2.83×10^{19}	51.6	0.0180	$<10^{-3}$[d]	2.3
7.7	7.3	9.9	1.12×10^{19}	7.2	0.0054	$<10^{-3}$[d]	1.7

[a] Plutonium was 4.78% ^{238}Pu; V = 1.09 L; T = 22 ± 1°C.

[b] Calculated from eq 4 with estimated value for k_r.

[c] Estimated from Figure 9.

[d] At these pressures and dose rates, it was assumed that the reverse reaction did not influence the PuF_6 pressure decreases.

TABLE V: Beta Radiolysis Experiments in Which PuF_6 Decomposition Was Measured at Two Times[a]

PuF_6 pressures, torr		Final total pressure, torr	Total decomposition, time days	Absorbed dose rate, eV/(torr•day)	Fractional dose rate contribution, %		$G(-PuF_6)$
Initial	Final				From Alpha	From Wall	
41.0	33.1	38.5	35.7	2.13×10^{19}	7.0	<1.0	0.89
25.4	18.8	24.4	69.1	2.04×10^{19}	4.0	<1.0	0.66
20.2	14.3	19.5	56.0	2.12×10^{19}	3.3	5.8	0.88
11.3	6.90	11.2	80.9	1.86×10^{19}	2.0	<1.0	0.93
9.60	5.10	8.95	80.9	1.78×10^{19}	1.6	<1.0	1.2
9.08	7.27	8.85	54.9	1.82×10^{19}	<1.0	<1.0	0.71
6.42	4.42	6.57	55.8	1.68×10^{19}	1.0	<1.0	1.2
5.04	2.06	5.11	66.8	1.92×10^{19}	1.0	25.0	1.5

[a] Plutonium was 72.92% ^{241}Pu; V = 1.09 L, T = 22 t/°C.

TABLE VI: Beta Radiolysis Experiments in Which PuF_6 Decomposition Was Measured at One Time[a]

PuF_6 pressures, torr		Final total pressure, torr	Decomposition time, days	Absorbed dose rate, eV/(torr•day)	Fractional dose rate contribution, %		G(-PuF_6)
Initial	Final				From Alpha	From Wall	
43.4	41.1	6	6.8	2.33×10^{19}	8.0	<1.0	1.2
19.9	17.7	20.2	18.0	2.02×10^{19}	2.6	<1.0	1.1
9.22	8.71	6	14.1	1.00×10^{19}	2.0	<1.0	0.79
8.84	8.02	8.96	17.6	1.83×10^{19}	1.7	<1.0	1.0
4.40	4.03	6	21.8	1.59×10^{19}	1.0	<1.0	0.93

[a] Plutonium was 72.92% ^{241}Pu; V = 1.09 L, T = 22 t/°C.

TABLE VII: k_f and k_r Calculated from Alpha Radiolysis Data of Steindler et al.[7]

Initial PuF_6 pressure, torr[a]	k_f, $(days)^{-1}$	k_r, $(days)^{-1}$
100	0.0024	0.0061
50	0.0012	0.0021

[a] Plutonium was 93% ^{239}Pu; V = 0.13 L; T = 26°C.

LIST OF FIGURES

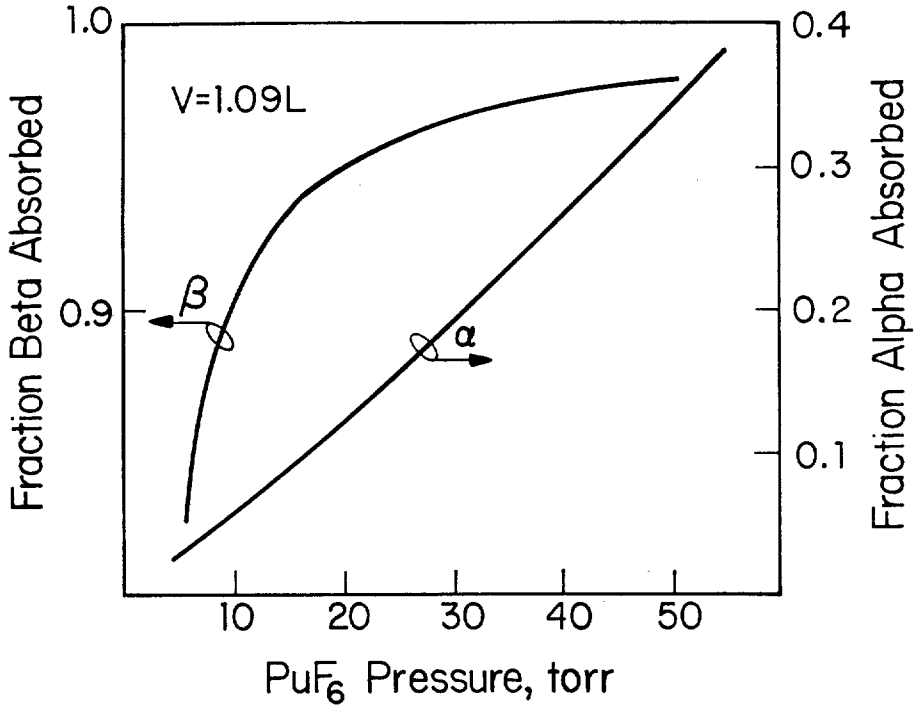

Figure 1. Fraction of alpha or beta energy absorbed by PuF_6 from particles emitted by plutonium in the vapor phase.

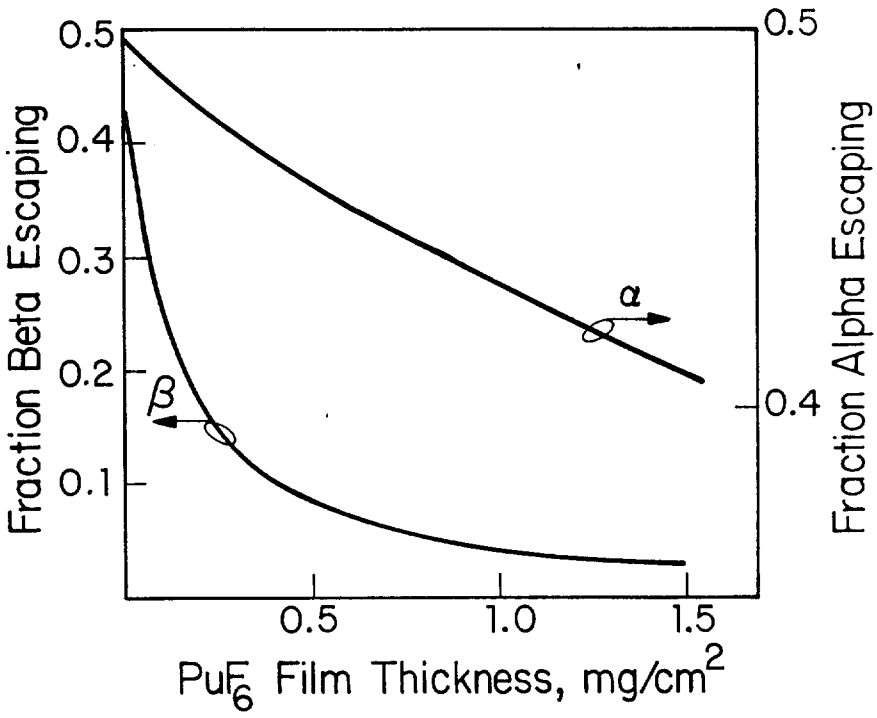

Figure 2. Fraction of alpha or beta particles that escape the vessel wall and the PuF_4 film.

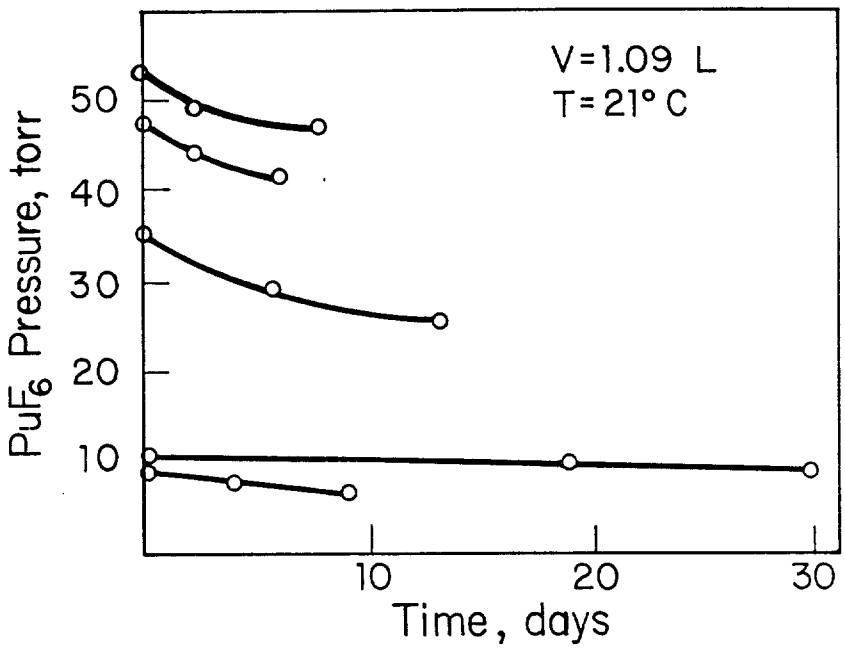

FIGURE 3. PuF_6 pressure decreases from alpha radiolysis. Plutonium was 4.78% ^{238}Pu.

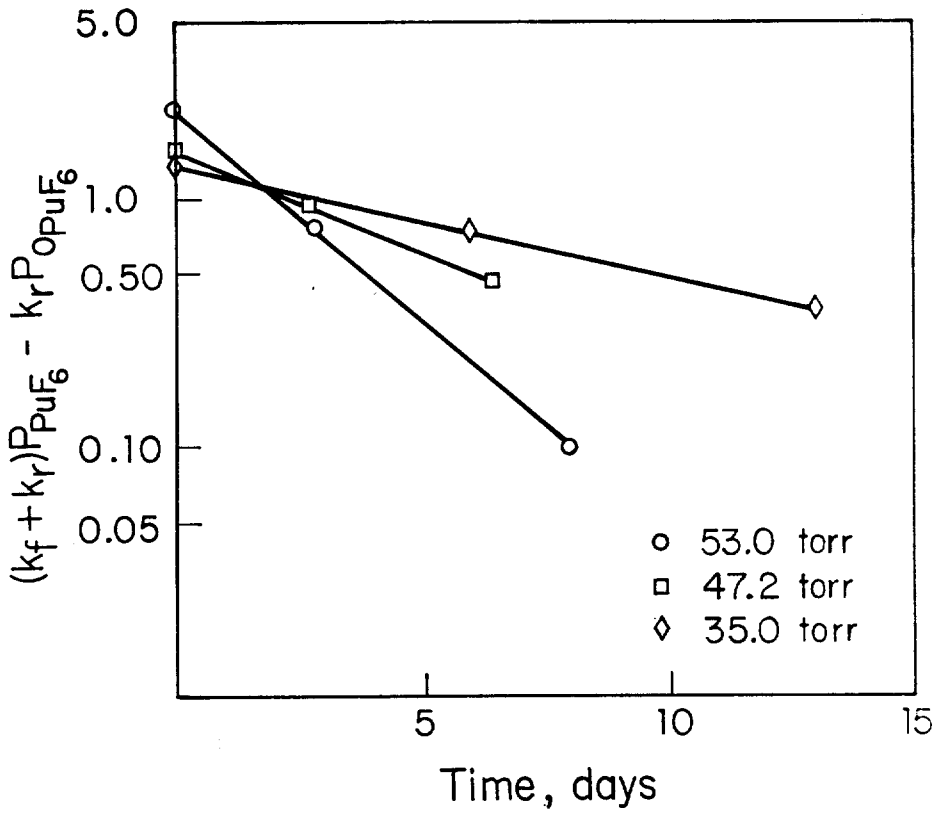

Figure 4. Correlation of alpha radiolysis data with first order reversible rate law.

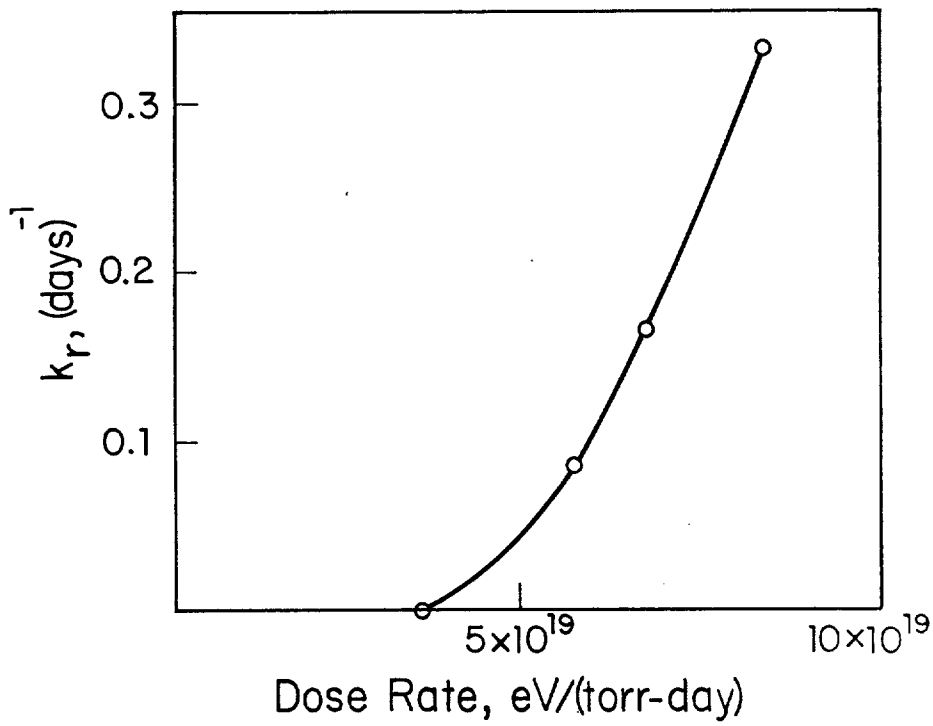

Figure 5. Variation of k_r with dose rate.

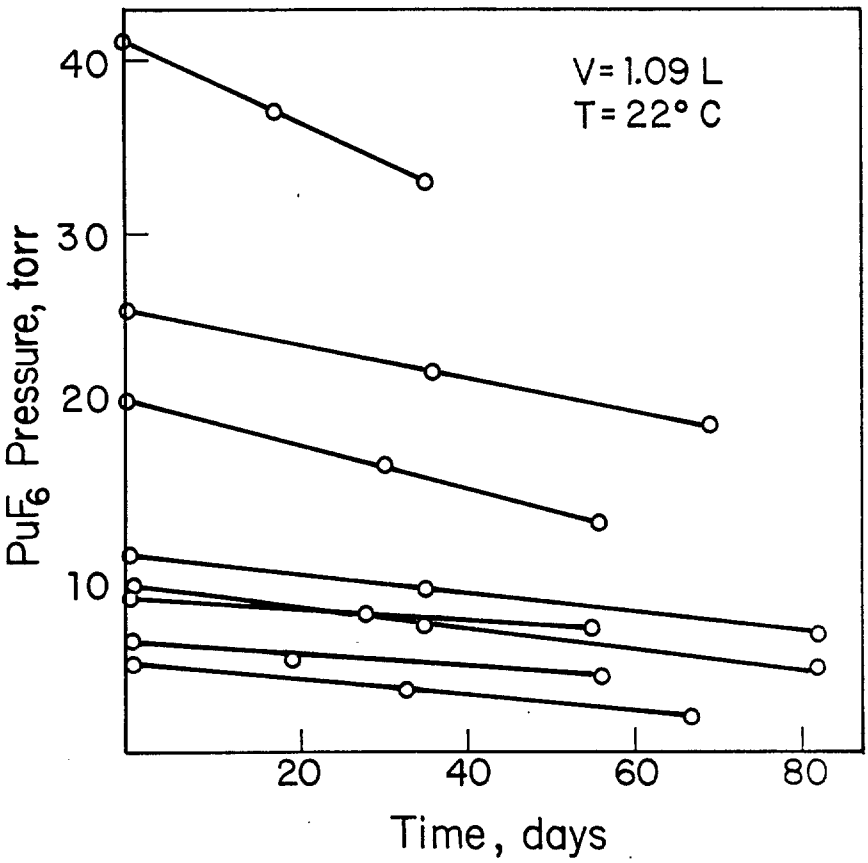

Figure 6. PuF_6 pressure decreases from beta radiolysis. Plutonium was 72.92% ^{241}Pu.

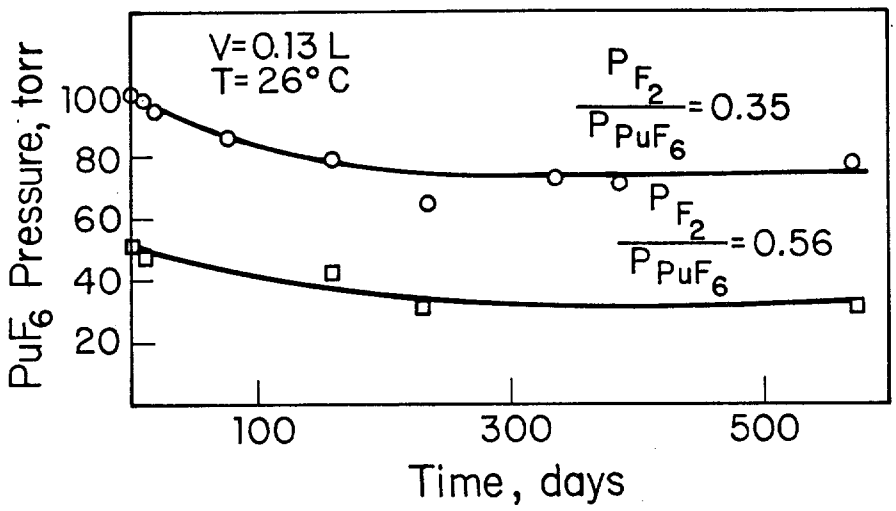

Figure 7. PuF_6 pressure decreases from alpha radiolysis (Reference 7). Plutonium was 93% ^{239}Pu.

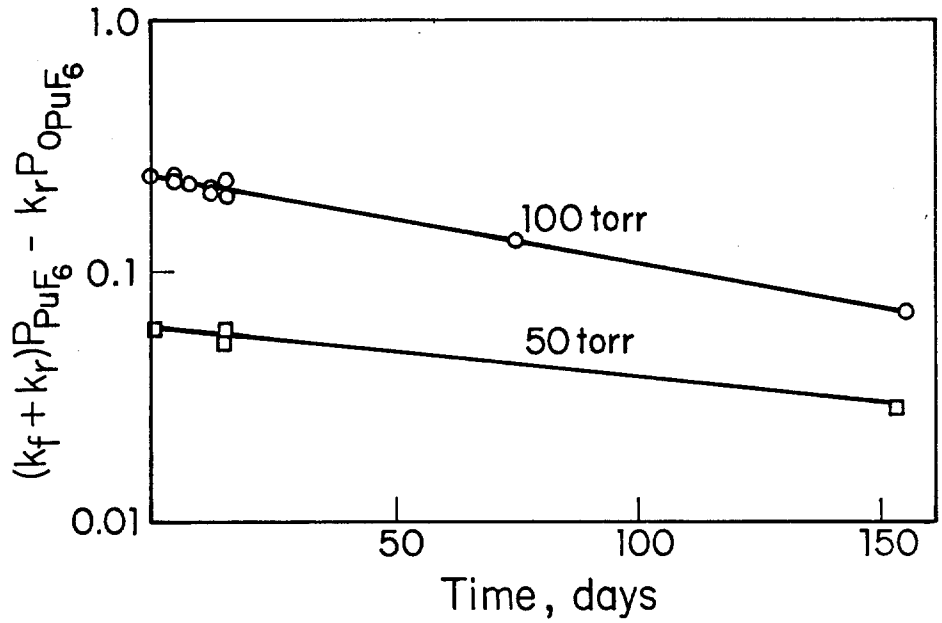

Figure 8. Correlation of alpha radiolysis from Reference 7 with first order reversible rate law.

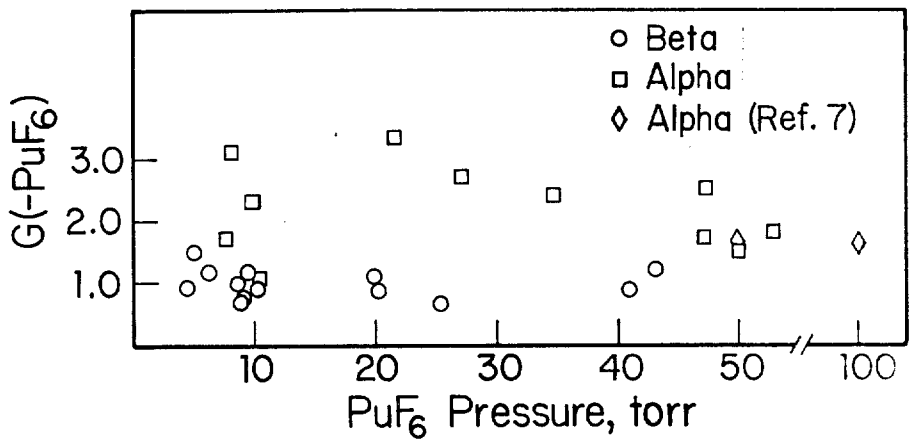

Figure 9. Correlation of alpha and beta radiolysis data.